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GLASS TRANSITION TEMPERATURE MEASUREMENT FOR UNDERCURED CYANATE ESTER NETWORKS: CHALLENGES, TIPS, AND TRICKS

29 January 2014

**Josiah T. Reams¹, Andrew Guenther², Kevin R. Lamison¹,
Joseph M. Mabry²**

¹ERC Incorporated

²Aerospace Systems Directorate, Air Force Research Laboratory

Ph: 661/275-8020; e-mail: andrew.guenther@us.af.mil



Outline



- Background:
 - What Does “Cured” Mean?
 - Importance of T_G : More Than Just Ceiling Temperatures
- Why can it be difficult to measure T_G ?
 - “High T_G ” + Easy to Process = Sensitivity
 - Vitrification + “Cure” = Undercure
 - Undercure + Sensitivity = Unstable T_G
 - “Blind to Chemistry” = Will Miss *In-Situ* Changes
- How to not miss a T_G



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Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

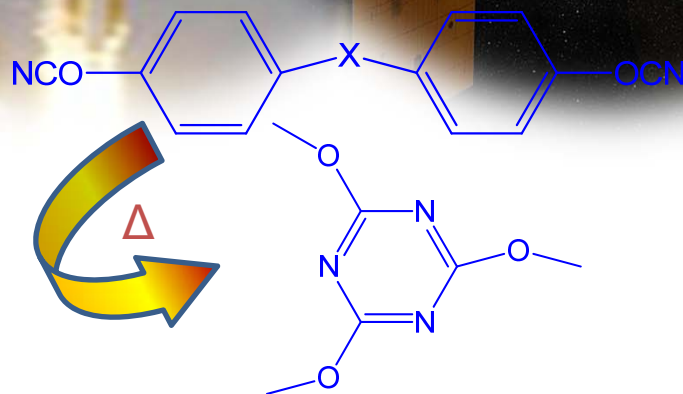
Onset of Weight Loss:
> 400 °C with High
Char Yield

Ease of
Processing

Resistance to
Harsh
Environments

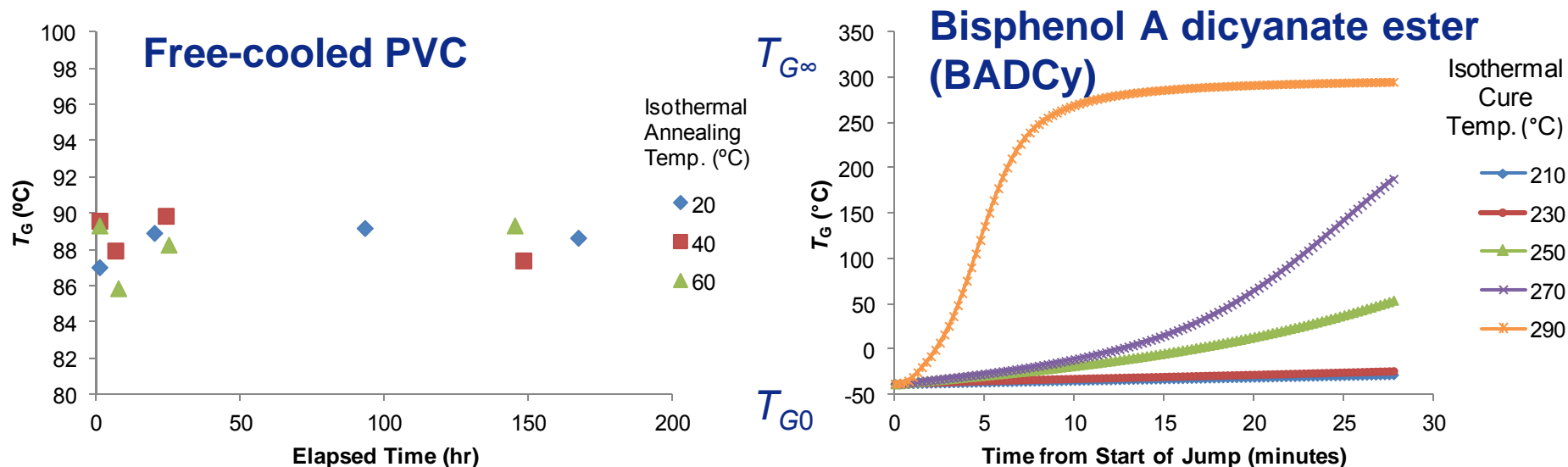
Good Flame,
Smoke, &
Toxicity
Characteristics

Low Water Uptake
with Near Zero
Coefficient of
Hygroscopic
Expansion





Thermosetting Polymers Have a T_G Envelope – Not Just a T_G

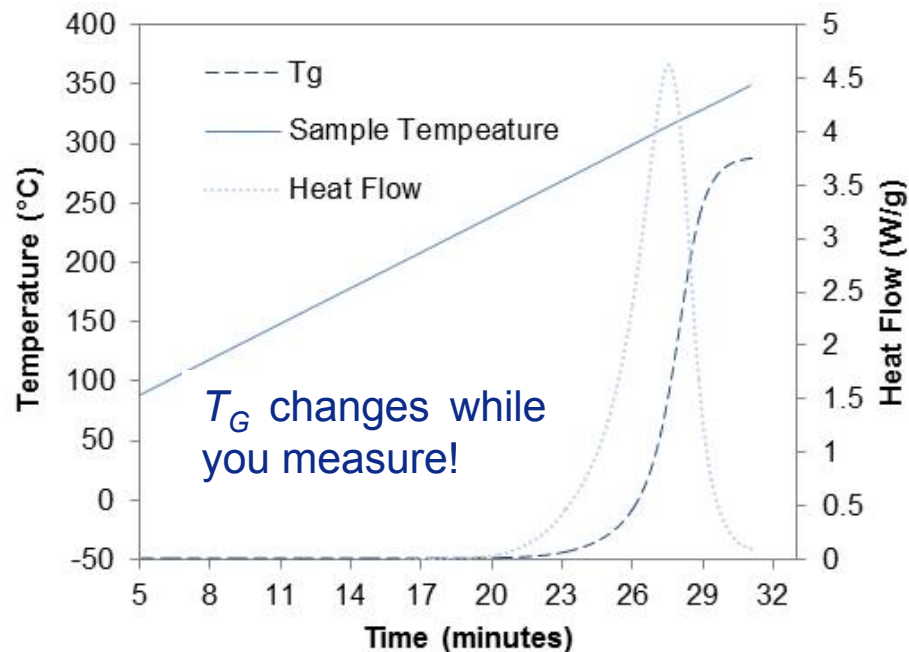
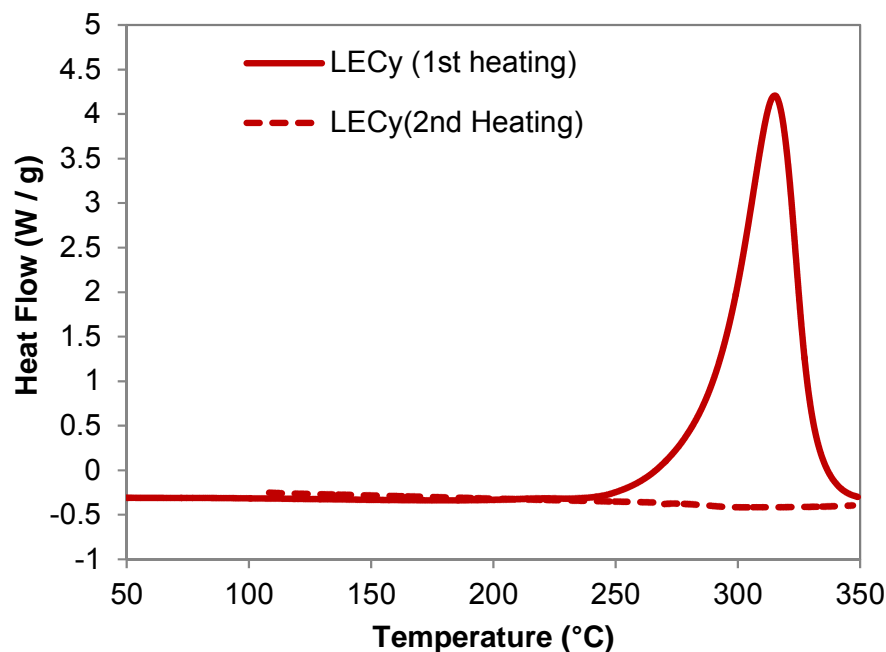


A. R. Berens and I. M. Hodges, *Macromolecules* **1982**, 15, 756 (digitized data from Fig. 2)

- The glass transition temperature of a thermoplastic such as PVC exhibits a nearly fixed value regardless of processing-induced changes to the system
- In contrast, the glass transition temperature of a thermosetting polymer can vary over a wide range of temperatures depending on how the polymer is processed
- A change in the extent of cure = a change in T_G



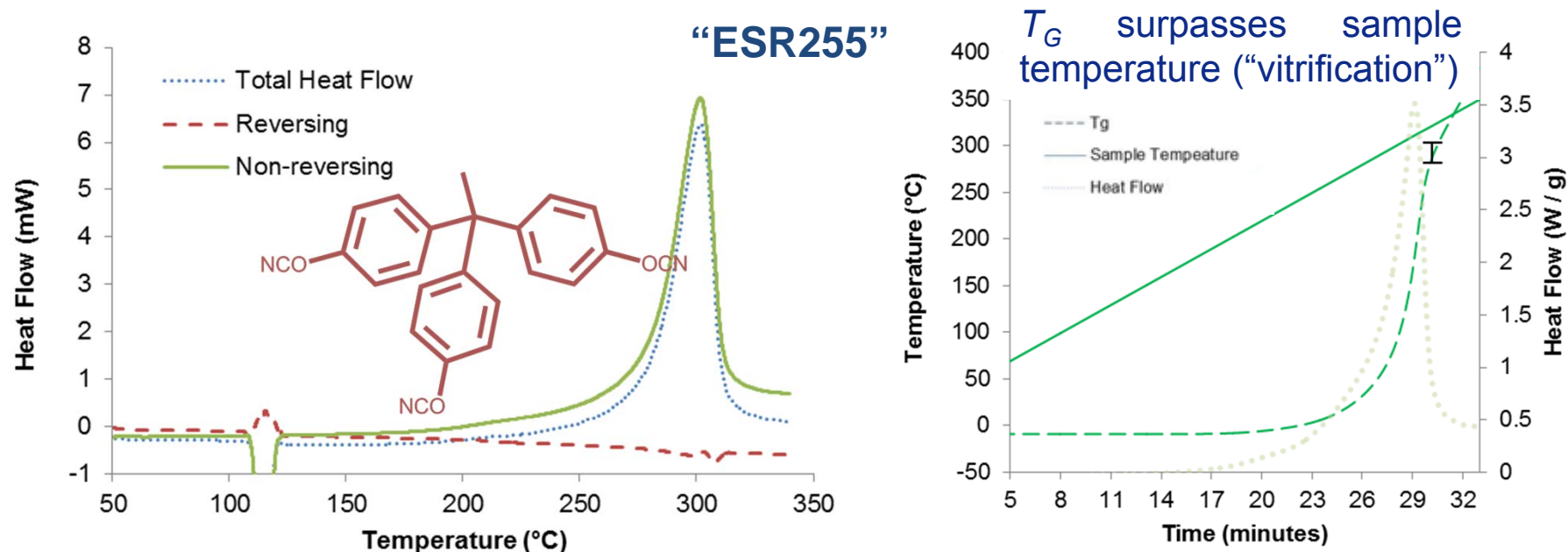
DSC + diBenedetto = T_g Estimated During the Scan



- In a thermosetting polymer with only one kind of network formation and negligible side reactions, the conversion may be determined at every point in the scan.
- By plugging the conversion into the diBenedetto equation, the T_g may also be determined at every point during the scan.
- Only when the sample temperature and T_g coincide is the T_g detectable (and even then it may be masked by cure).
- Just because no T_g is visible does not mean T_g lies outside the scan range.



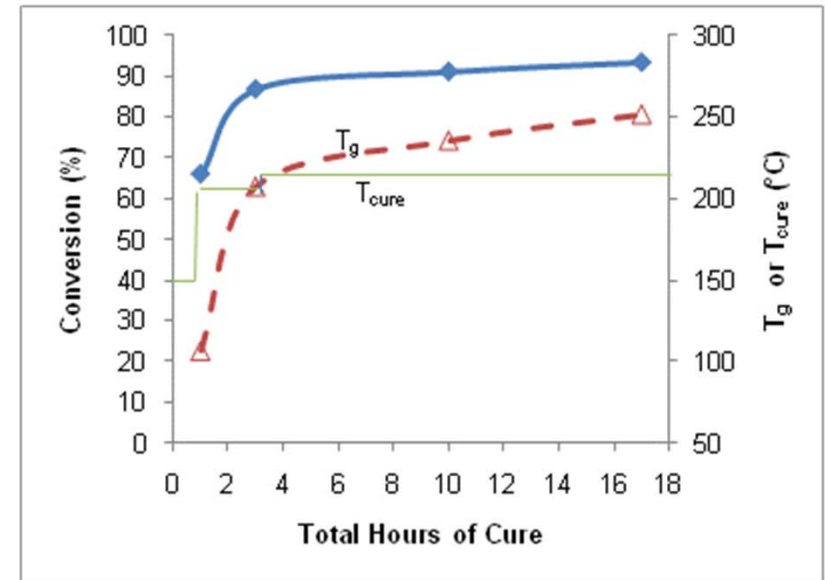
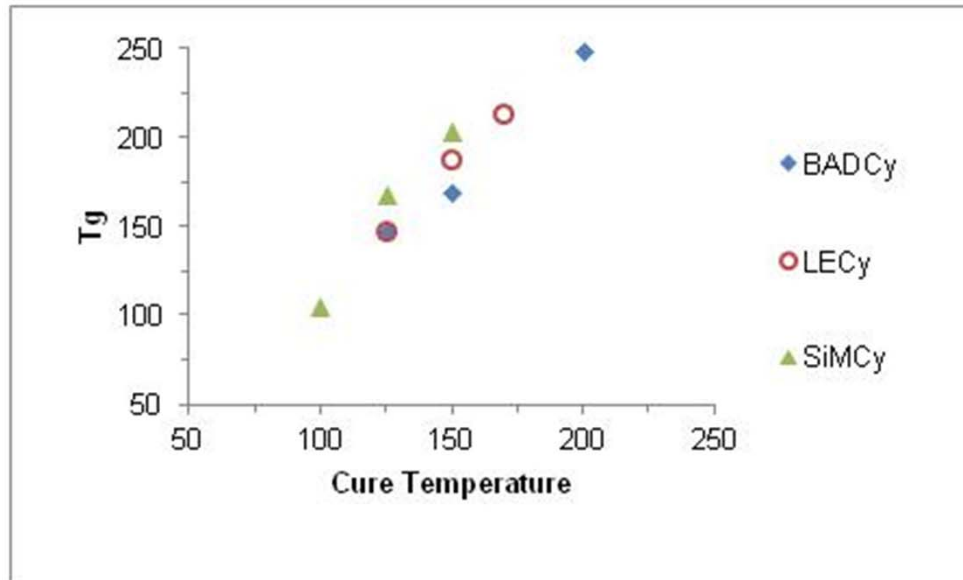
Vitrification Can Prevent Complete Conversion to Cyanurate



- In highly rigid cyanate esters, the T_G often increases beyond the cure temperature, leading to “vitrification.”
- Vitrification leads to a characteristic “L-shaped” DSC curve, which is often mistaken for a peak with a tilted baseline.
- To utilize the diBenedetto equation, FT-IR in combination with DSC is needed to measure conversion.
- **Modulated DSC** proves that cure is still in progress at the very end of the scan.



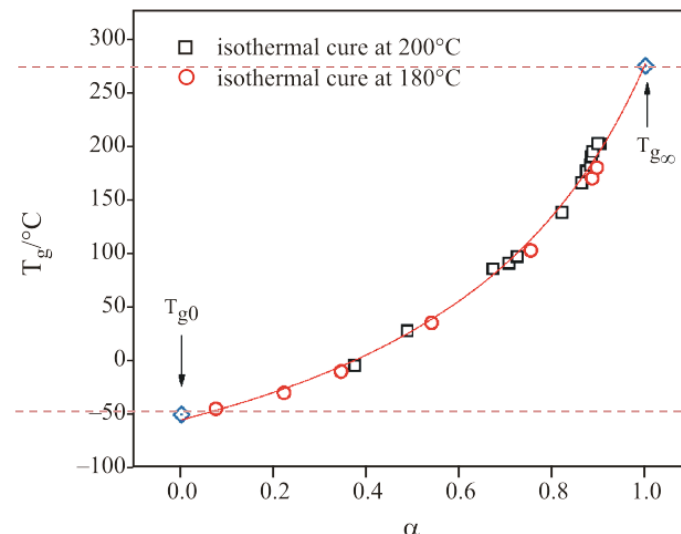
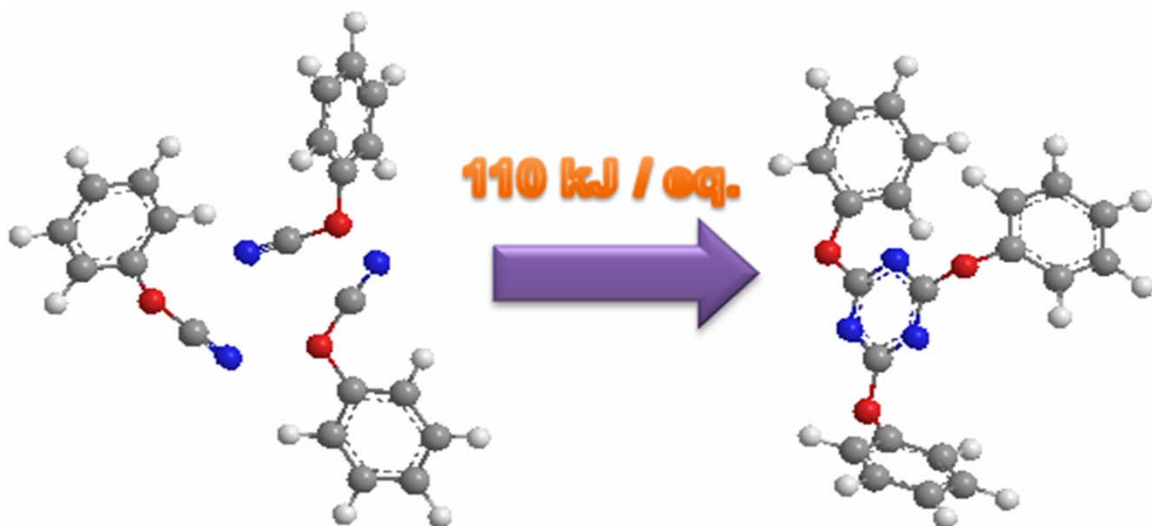
“Cured” Cyanate Esters Are Usually Just Vitrified Samples



- When conversion exceed about 65%, vitrified samples have the same physical appearance and handling characteristics at room temperature regardless of the extent of cure.
- Vitrification implies that isothermal cure is very slow, but the “L-shaped” DSC indicates that significant marginal cure is achieved by heating the sample.
- **Whenever a vitrified sample is heated to a temperature between $\sim T_{cure}$ and $T_{G\infty}$ for the first time, it will undergo additional cure, increasing T_G .**



Why Do Vitrified Cyanate Esters Cure Readily?



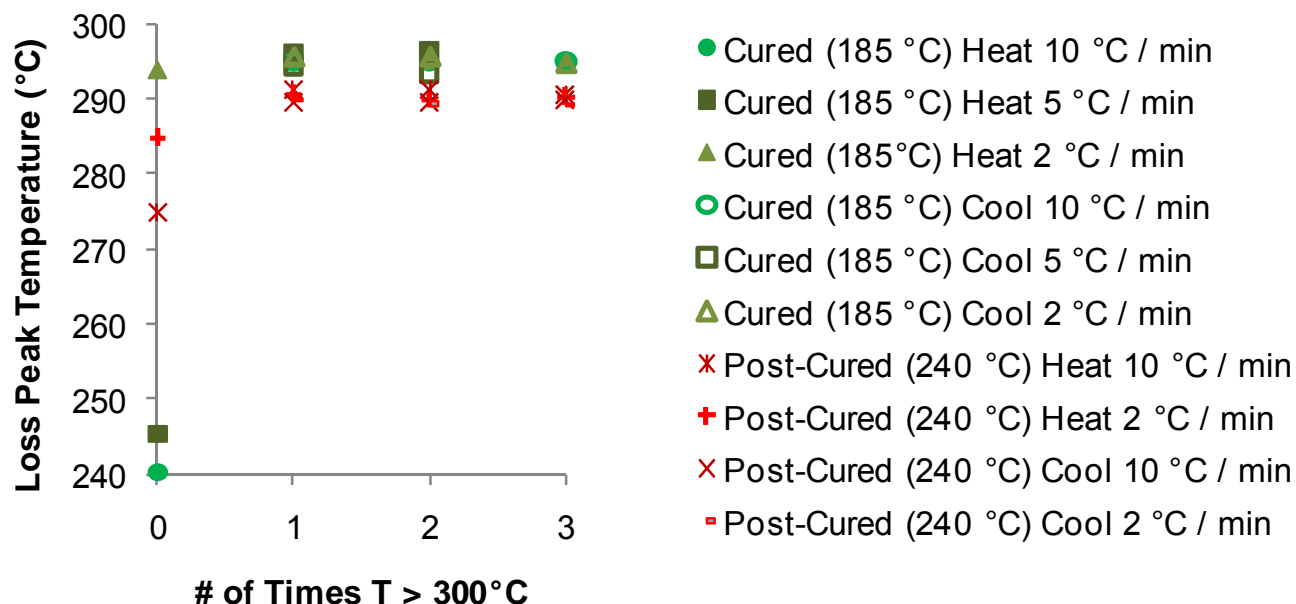
- Large enthalpy of reaction = high thermodynamic driving force (true of all stable, single-product cure systems)
- High sensitivity of T_g to conversion (true of all high-temperature, easily processed resins)
- Some facilitation of cure by catalysts is also possible.



Effect of Heating Rate on T_G of Vitrified LECy



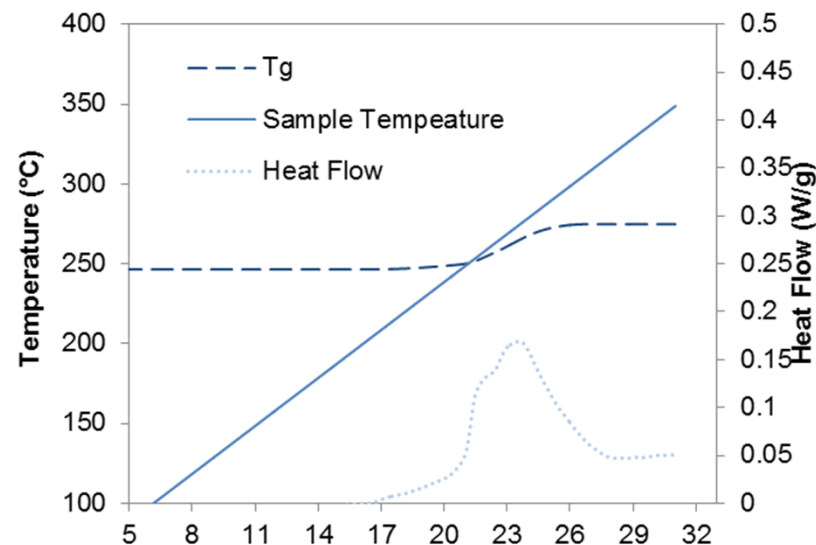
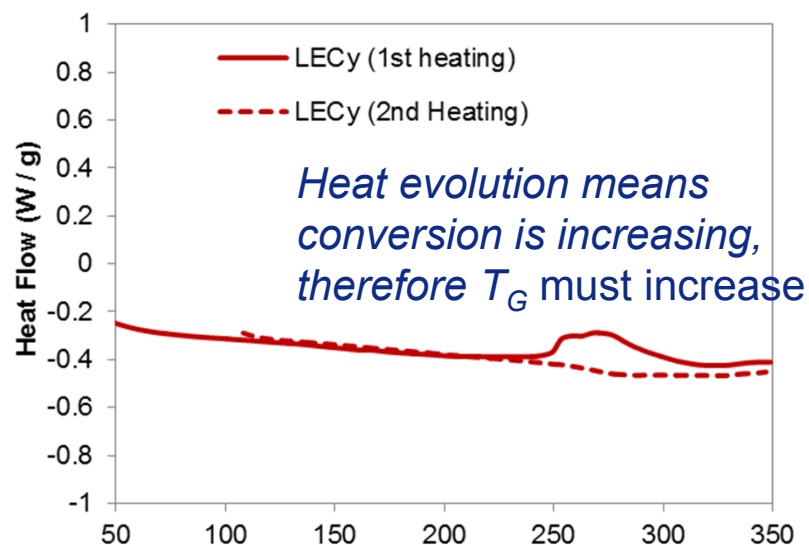
Primaset® LECY, Catalyzed



- Data shown are for multi-cycle dynamic TMA experiments
- $T_{G\infty}$ for catalyzed LECy reported at 290 °C (loss peak)
- Note how only samples that have not previously been above $T_{G\infty}$ show variability



DSC of Vitrified LECy (Cured @ 210 °C for 24 hours)



*LECy catalyzed with 160 ppm Cu
(as Cu-AcAc) + 2 phr nonylphenol*

The diBenedetto equation is used to find T_G assuming complete cure by 350 °C

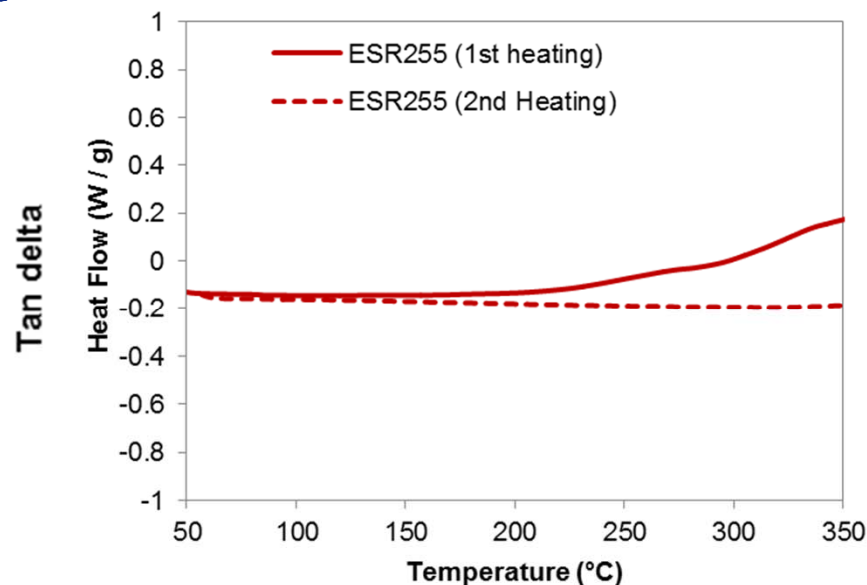
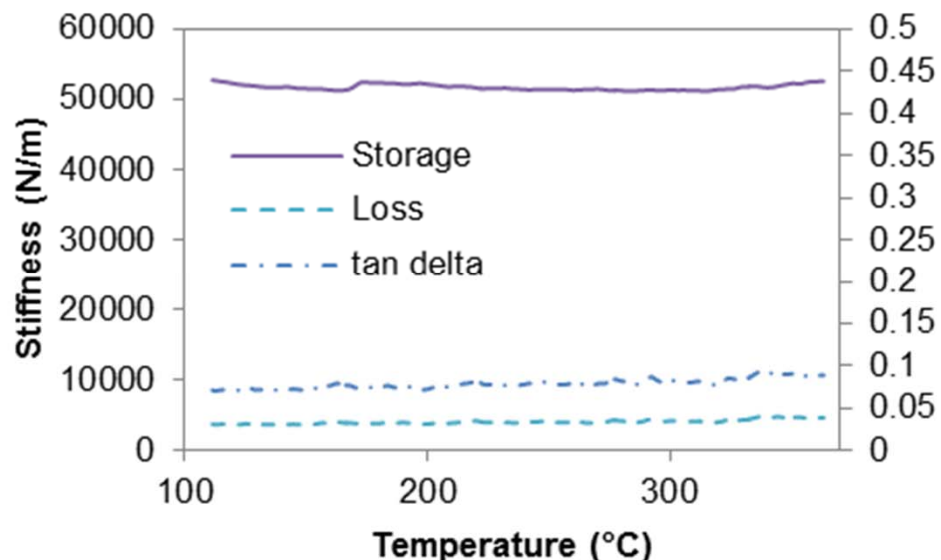
- Because the T_G begins to change just as the sample temperature and the T_G converge, the typical signal associated with a T_G in DSC scans is not observed.
- As soon as the vitrified sample nears T_G , it de-vitrifies, which allows cure to resume. The resumption of cure increases T_G , creating a situation in which the T_G changes as the sample temperature changes.
- In this case, the heating rate of 10 °C / min. is fast enough, and the rate of cure slow enough, that the T_G does not change much before it is measured.



Dynamic TMA and DSC Scans of Vitrified ESR255



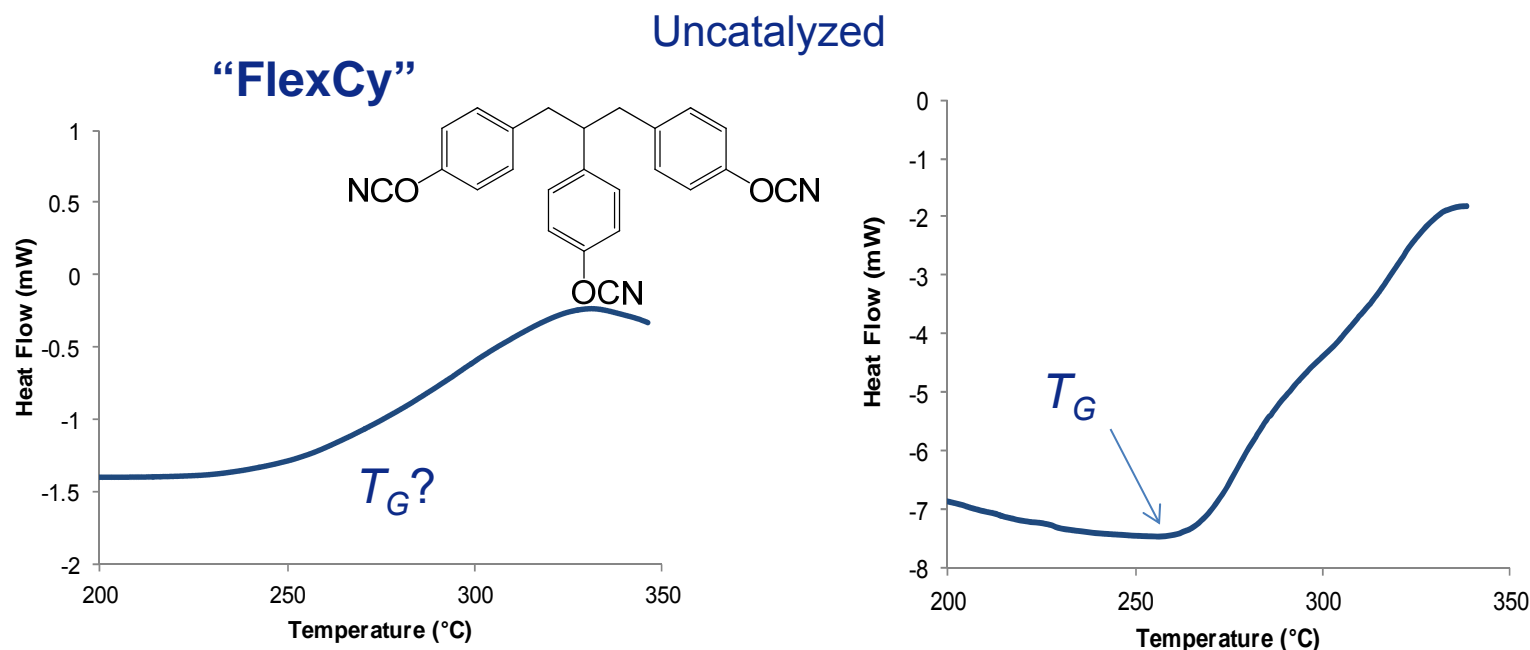
Uncatalyzed



- Sample cured at 210 °C for 24 hours
- While dynamic TMA (heating at 10 °C / min.) seems to indicate a very high “as cured” T_G , it cannot determine whether cure has taken place *in-situ*.
- DSC, however, at 10 °C / min. shows that cure starts at around 250 C, thus the T_G is changing while the measurement is taking place due to *in-situ* cure.
- Even though cyanate esters can cure at temperatures below T_G , a T_G exceeding the cure temperature by > 100 °C would be unprecedented.



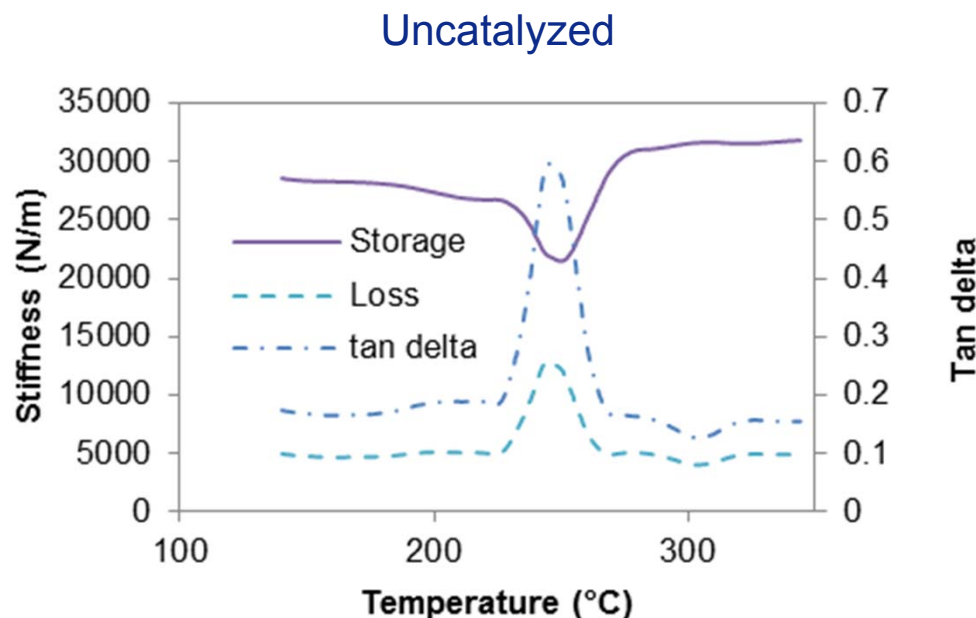
DSC Scans of Vitrified FlexCy at 10 °C / min. and 50 °C / min



- Note how much more distinct the transition between cure in the glassy and rubbery states is when using a rapid heating rate.
- At higher heating rates, there is less time available to cure in the glassy state, thus the T_G increases to a lesser extent, allowing the scan temperature to “overtake” it more suddenly.
- It is the sudden “cascade” of motion that makes the T_G appear clearly, as a “devitrification” rather than as a transition.



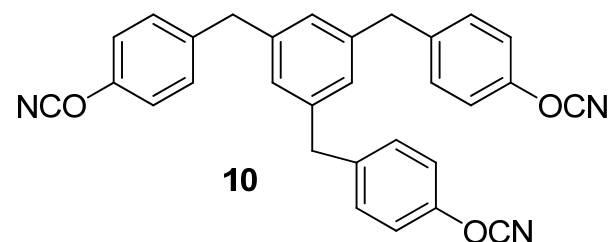
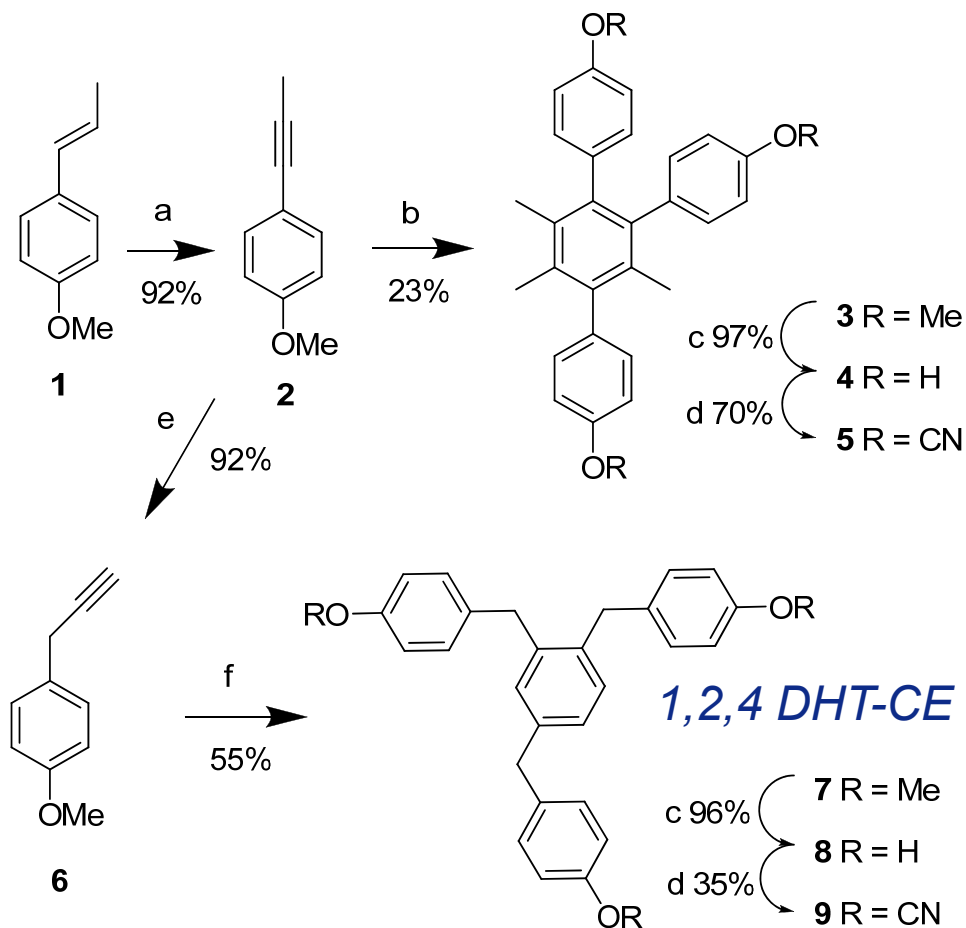
Dynamic TMA Scan @ 50 °C / min. of Vitrified ESR255



- Sample cured at 210 °C for 24 hours
- Heating at 50 °C / min. allows the sample to get close enough to the “as cured” T_G , that an initial drop in stiffness is recorded.
- Immediately afterward, however, cure resumes and takes place rapidly, pushing the T_G , well beyond the limits of the experiment (controlled by onset of degradation).
- Even very rapid heating rates may not stop *in-situ* cure.



Trianethole-Based Cyanate Esters and Related Compounds

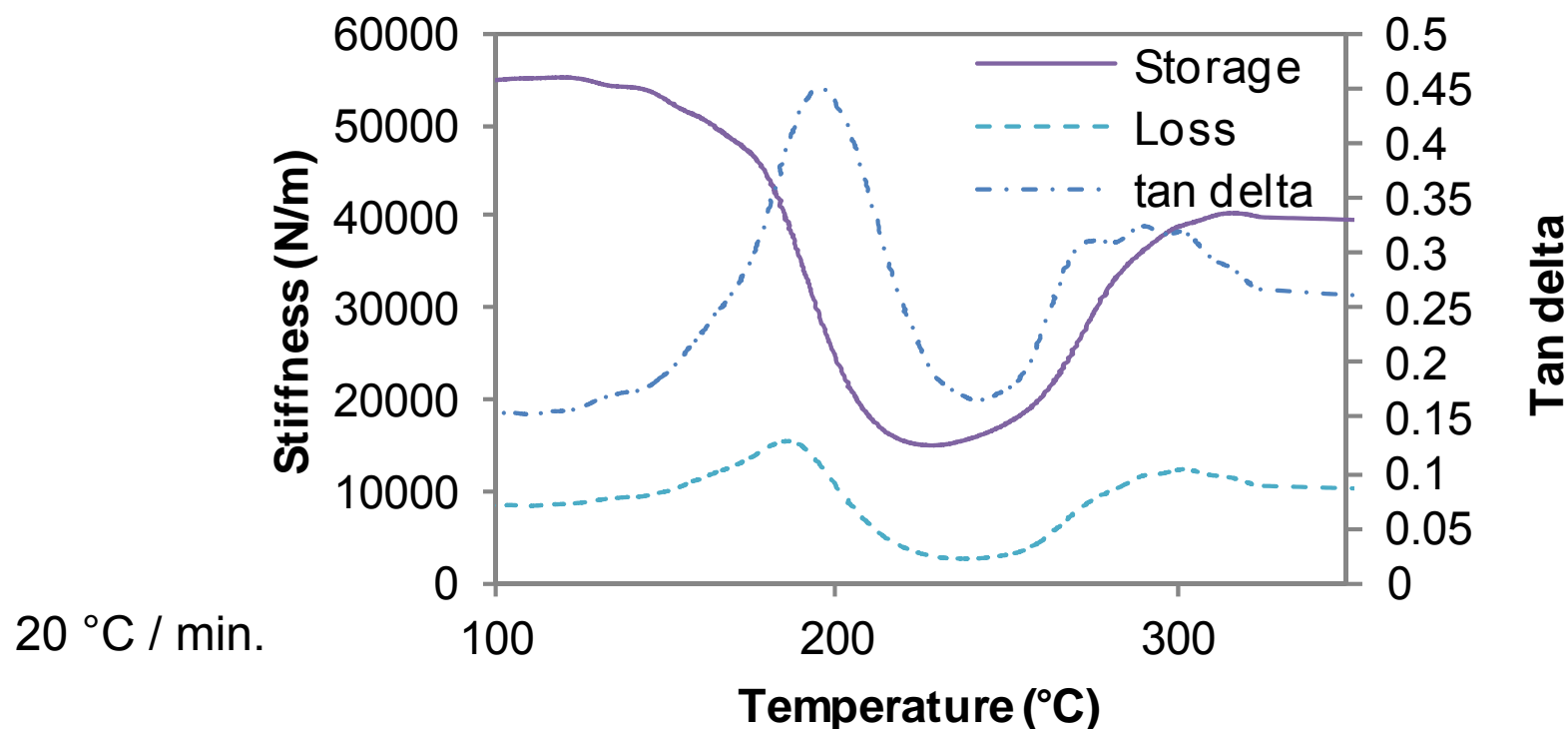


- Compound 10 is an isomer of compound 9 (1,3,5 vs. 1,2,4 substitution); all compounds were prepared by Dr. Matthew Davis at NAWCWD.

Reagents & conditions: a) 1. Br₂, THF, 0 °C; 2. KOtBu, THF, 0 °C to reflux; b) TMSCl, 5% Pd/C, dioxane, reflux; c) pyridine, POCl₃, H₂O, reflux; d) BrCN, TEA, acetone, -20 °C; e) BuLi, Et₂O, hexanes, rt; f) CoI₂, ZnBr₂, Zn, MeCN; g) pyridineHCl, reflux.



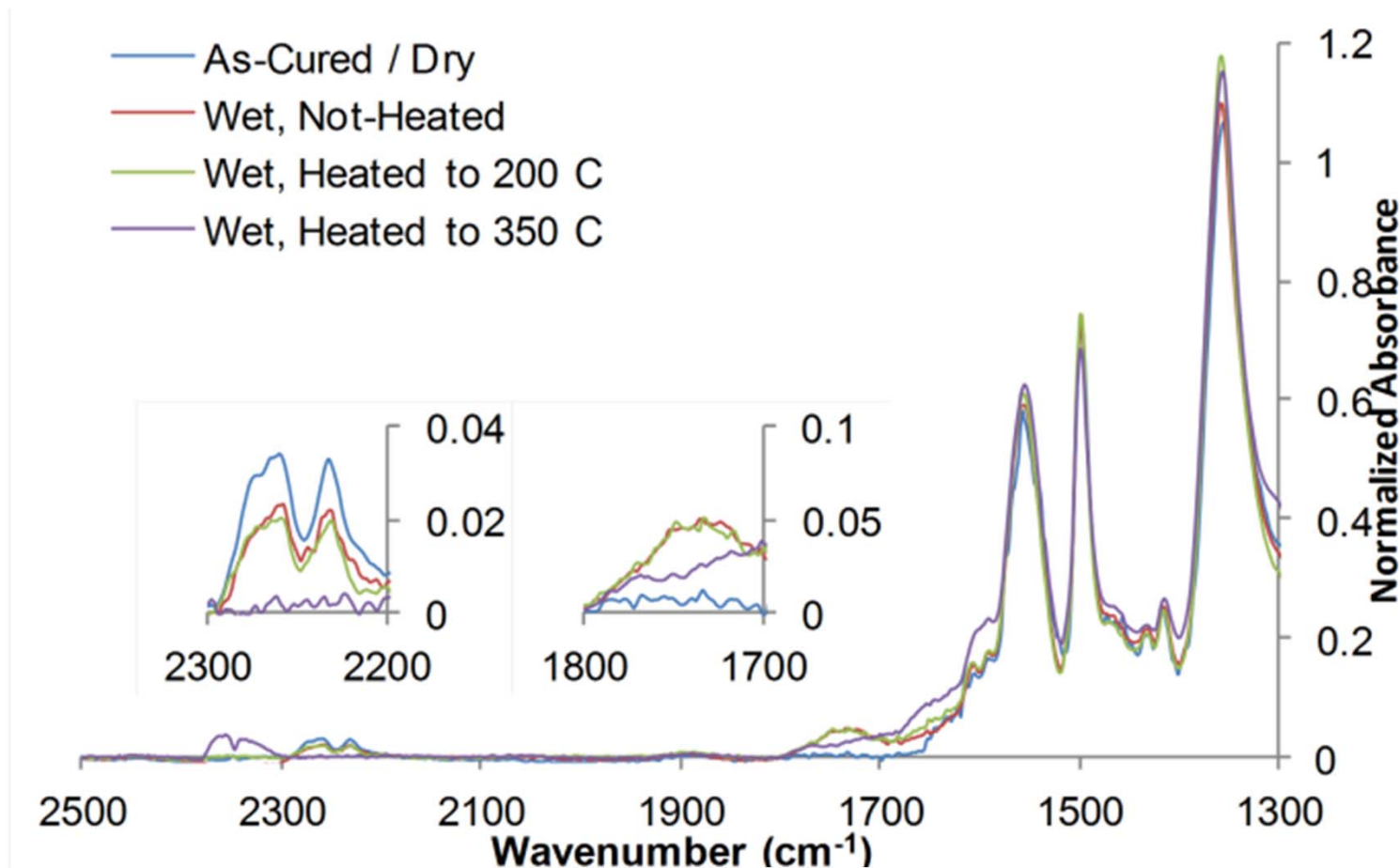
“Wet” TMA of 1,2,4 DHT-CE (80% Conversion Prior to Immersion)



- Sample cured at 210 °C for 24 hrs, then immersed in 85 °C DI water for 96 hrs.
- Samples retain 50-80% of the water weight gain after heating to 200 °C (FT-IR confirms –OH remains present), best guess is 2 mol water / 100 mol monomer – OCN.
- FT-IR confirms increase in stiffness due to *in-situ* cure, not drying. Dry $T_g = 235$ °C.



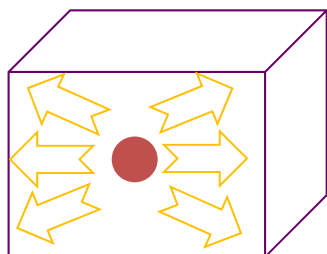
FT-IR Data on Wet 1,2,4 DHT-CE (87% Conversion Prior to Immersion)



- Careful sample prep + high # of scans = quantifiable results!
- Residual –OCN to carbamate conversion, and destruction of carbamate clearly seen.



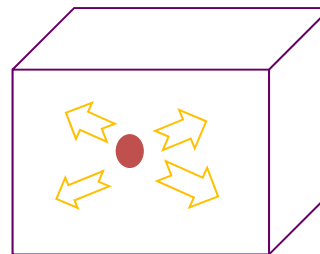
Bubble Growth in Wet Resin Samples



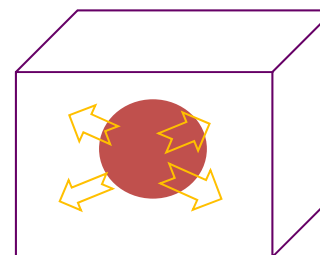
Bubble Forms, creates pressure gradient in matrix

Growth criteria:
 $r^2 P^* \phi / \mu D > \sim 1$

Note: μ is practically infinite for $T < T_G$



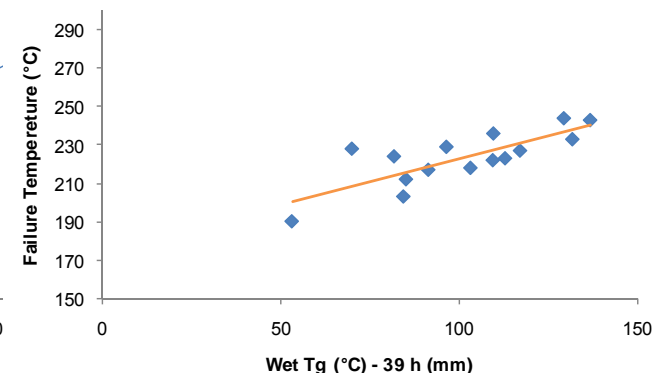
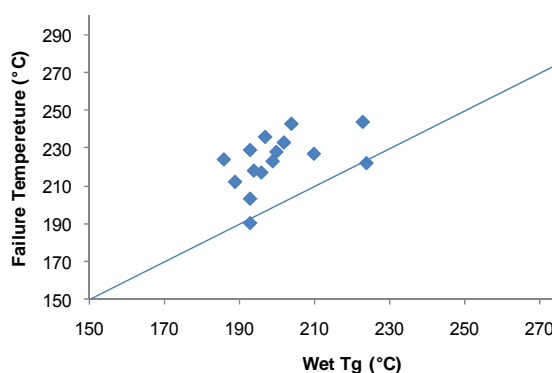
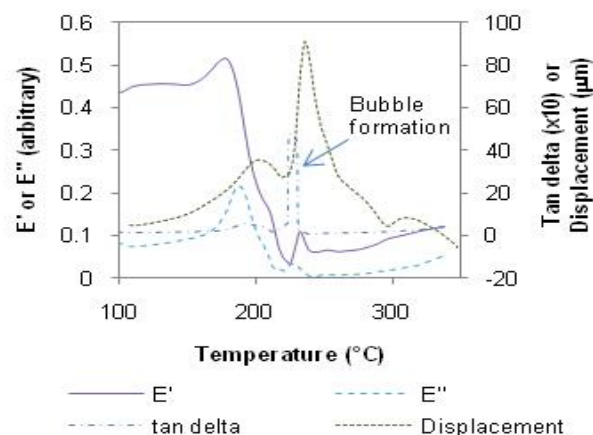
$T < T_G$



$T > T_G$

High modulus resin contains pressure; diffusion quickly dissipates bubble; cracks may initiate.

Lower modulus resin yields and flows, allowing bubble to grow; new gas swept into bubble counters pressure drop.





Comparison of Dry and Wet TMA Measurements of T_G



Dry TMA



- ☐ Often requires heating well past final cure temperature
- ☐ Inert, dry conditions favor *in-situ* cure
- ☐ “Blind” to chemical changes
- ☐ No cascade effects to help identify T_G

Wet TMA



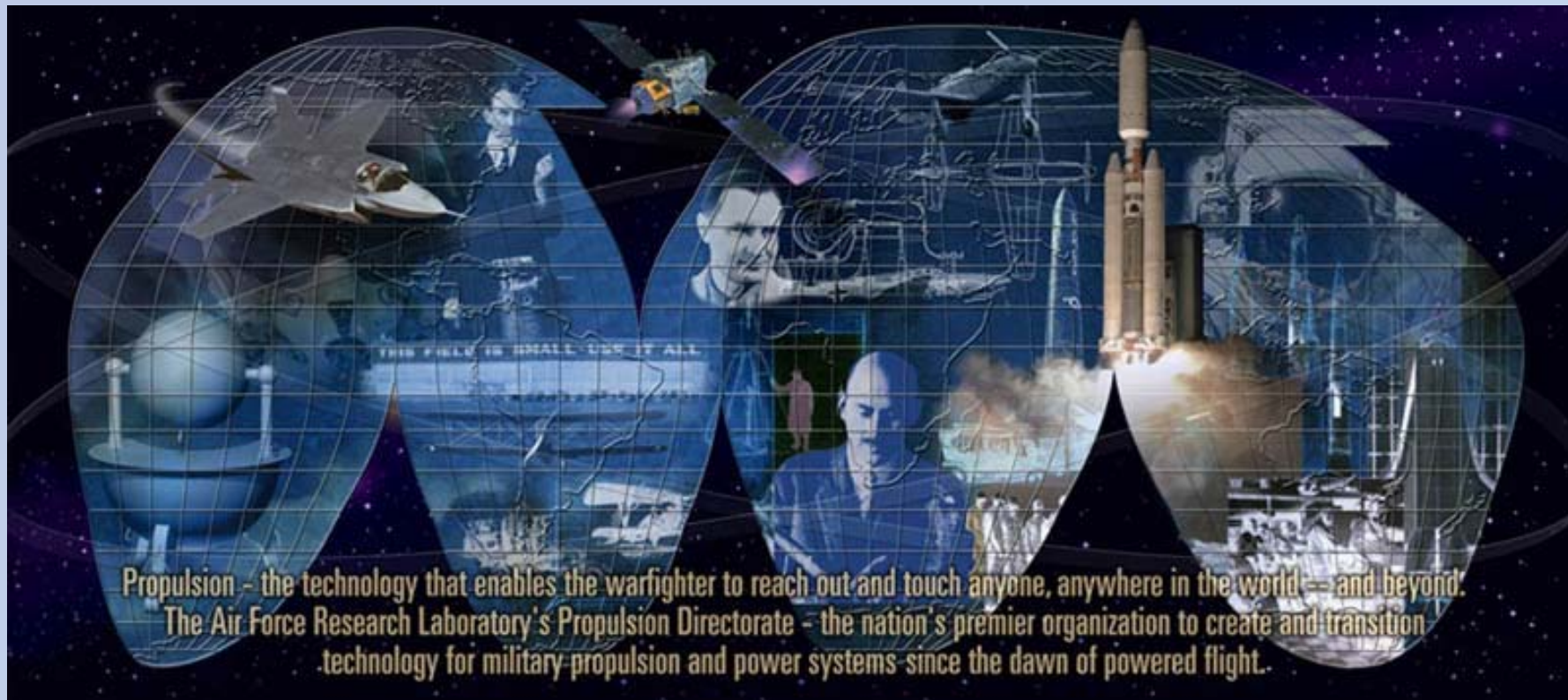
- ☐ Plasticization and degradation drop T_G to near / below cure temperature
- ☐ Carbamate formation dilutes remaining $-OCN$ groups, slows down *in-situ* cure
- ☐ Bubble formation can confirm system is above T_G
- ☐ Must consider geometry and mass transport effects

- Lists applicable to cyanate esters only; effects on other resins depend on the nature of the cure chemistry.



Summary

- The attainable T_G in a cyanate ester thermosetting resin is not a fixed quantity but varies over an envelope determined by the degree of conversion and the limits of mechanical and chemical stability of the cure network, so the T_G can change while you attempt to measure it.
- Because most “cured” cyanate ester samples are really undercured but vitrified, they tend to cure quickly whenever heated past their previous maximum cure temperature. Additional cure will always increase the T_G . Thus, performing an ASTM standard test for T_G on a “cured” cyanate ester is an excellent way to make the T_G change while you attempt to measure it.
- The best way to measure T_G is to find a technique that is sensitive to an irreversible cascade effect; the onset of heat given off by residual cure in a DSC with a fast heating rate is an excellent way to accurately measure an “as cured” T_G .
- Interestingly, for cyanate esters, the effects of water exposure, including a drop in T_G to near or below the final cure temperature, conversion of residual $-OCN$ to carbamate, and bubble formation make it easier to measure T_G in wet samples, despite the important mass transfer effects.



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